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A battery with miniaturised SOFC fuel cells

The invention relates to a battery with miniaturised SOFC fuel cells (SOFC: solid oxide fuel cell). The battery contains the fuel cells in the form of a multi-modular unit, in particular in the form of a stack, the volume of which is preferably less than $10^{-4}m^3$. The invention also relates to a method for operation of the battery as well as for uses for the battery.

Portable electronic devices are at a stage of development in which these devices are becoming increasingly complicated and are being integrated into systems which are more and more complex. Due to the increase in complexity the need for electrical energy for operating the devices or systems is growing all the time. Conventional batteries, which are reloadable, reach the limits of their capacity. Therefore batteries with miniaturised fuel cells are suggested, with which the named limits of capacity can be exceeded. Since batteries of this kind have to be relatively small, it is difficult to use electrochemical processes, which take place at high temperatures. For this reason miniaturised fuel cells are being developed, which work with polymer membranes at low temperatures (cells of the type PEMFC: proton exchange membrane fuel cell). In membranes of this kind a minimum water content has to be maintained however. This requirement is difficult to fulfil. Hydrogen is used as a fuel, which is a disadvantage with regard to storage, since only relatively small energy densities are possible with stored hydrogen.

Due to the problems with the PEMFC fuel cells, SOFC fuel cells have also been suggested, in spite of the known difficulties (see for example WO

0243177). In these fuel cells the membranes are made of solid electrolytes, which only have sufficiently high ionic conductivity at temperatures higher than 500° C. Propane or butane, which advantageously have relatively high energy densities in liquid form, can be used as fuels for example.

The object of the invention is to produce a further battery with miniaturised SOFC fuel cells, which can be used as a mobile source for electrical energy. This object is solved by the battery defined in claim 1.

The battery with miniaturised SOFC fuel cells includes the following components: a stack made up of the fuel cells or another multi-modular unit, with a volume which is less than $10^{-3}m^3$, preferably less than $10^{-4}m^3$; a channel system in the channels of which on the one hand reactants, namely gaseous fuel and also air can be fed to the cells and on the other hand the fuel, which is partially depleted in the cells, can be subjected to afterburning; a casing, which is made at least partially heat insulating; a heat exchanger, which is part of the channel system and in which the air supplied can be heated up with exhaust gas; an apparatus for feeding the air; an exchangeable or refillable reservoir for the fuel, which is stored in this at a pressure, which is greater than the environmental pressure and in which the fuel is preferably liquid; controlled valves in connection lines for the reactants; and a control. The afterburning is not necessarily required. The fuel cells respectively contain a disc-shaped solid electrolyte, which in addition to ion conducting components also includes electron conducting components, which cause an ohmic loss. In this the quantity ratio of these components is so designed that in an idling operation of the battery a heat flow from the cells to the environment can be compensated by the ohmic loss.

The dependent claims 2 to 6 relate to advantageous embodiments of the battery in accordance with the invention. Methods for operating the battery in accordance with the invention are subject of the claims 7 to 8 respectively. Claim 9 relates to a use of the battery.

In the following the invention is explained on the basis of the drawings. They show:

Fig. 1 an overview of the components of a battery in accordance with the invention,

Fig. 2 a cross-section through a part of a fuel cell,

Fig. 3 a schematic view of the electrical connections of the cells,

Fig. 4 a section through a cell stack with a view of the anode,

Fig. 5 a section through a cell stack with a view of the cathode and

Fig. 6 an apparatus for the feeding of the air.

The overview given by Figure 1 shows the following components of a battery 1 in accordance with the invention: a cylindrical stack 20 with fuel cells 2; an apparatus 4 for the transport of air; a heat insulating casing part 10, which is shown as a longitudinal section; an exchangeable or refillable reservoir 5 for a fuel 50; a heat exchanger 6; a condenser 7, a shell-like casing part 11, which can be plugged on to the heat insulating casing part 10 (plug region 101). The casing parts 10 and 11 are advantageously made of metal. If the casing parts 10 and 11 are electrically sepa-

rated with an insulation in the plug region 101, then - with suitable connections 70 and 71 at the condenser (for example) - they can be used as poles 12 and 13 of the battery.

The fuel cells can also form another multi-modular unit instead of a stack 20. In a multi-modular unit of this kind the cells 2 can for example be arranged in one layer or in at least one layer next to each other (not shown).

The fuel 50 (Fig. 2) can be let out of the reservoir 5 via a controllable valve 51 into a central distributing tube 25 of the cell stack 20. The battery component for a control is not illustrated. The reservoir 5 is exchangeable or refillable. The fuel 50 is stored at a pressure, which is greater than the environmental pressure and in which the fuel 50 is advantageously present as a liquid phase. The battery 1 in accordance with the invention includes a channel system, into the channels of which the reactants, on the one hand, namely the gaseous fuel 50 and also the air 40, can be led to the cells 2 and, on the other hand, a the fuel, which is partially depleted in the cells 2 can be subjected to afterburning. The afterburning can be carried out catalytically at temperatures higher than 250°C.

In the described embodiment the solid electrolyte is circular. The cell stack 20 can also be of prismatic form, for example with a quadratic base surface, so that the solid electrolyte must have a correspondingly quadratic shape. Instead of the separate apparatus 4 for transporting the air 40, other transport means are also possible, namely for example a system of jets integrated in the cell stack 20, in which the gaseous fuel can be used for the air transport, using its pressure as the driving power.

In Fig. 2 section of a part of the fuel cell 2 lying to the left of a middle line 15 i.e. of the central axis of the stack 20 is shown. This cell is made of a structured part 2a, a second structured part 2b and an electrochemically active element 3, which includes a membrane 30 of a solid electrolyte and also two layer-like electrodes, namely a cathode 34 and an anode 35. The architecture of the two parts 2a and 2b can be seen in the Figures 4 and 5. They form mechanically stable support structures for the solid electrolyte membranes 30, which are homogenous and unstructured and can preferably be manufactured from mono-crystalline silicon. This material is structured by means of micro-technical methods, in particular etching methods (for example "back-etching" of the part 2b on the anode side. See for example the already named WO 0243177).

Neighbouring cells 2 and 2' (shown in chain-dotted lines) are respectively arranged in relation to one another in mirror symmetry, so that electrodes 34 and 35 of the same name cover the inner surfaces of common electrode gas chambers for the air 40 or for the fuel 50. Fig. 3 shows how in this arrangement, the electrodes 34 or 35 have to be connected with each other electrically in order to maintain a series circuit, for which terminal voltage between the poles 12 and 13 is equal to the sum of the individual voltages of the electrochemically active elements 3.

During operation of the battery the air 40 is distributed through axial channels 24, which are arranged in the peripheral region of the cells 2: see Figures 2 and 5. The air 40 flows into the cells 2 initially radially from feed points 24' radially towards the central axis 15 and is then steered back to the periphery. The oxygen ions migrate through the solid electrolyte membrane 30 to the anode 35, where they react with the fuel 50 giving up the excess electrons to form water H_2O and CO_2. The fuel 50, which is distributed by means of the central channel 25, reaches the

electrode gas chambers lined with the anodes 35, via radial channels 25': see Figures 2 and 4. After the transport through the electrode gas chambers, the air 40 and fuel 50 enter common channels 26, which are axially arranged between the air channels 24 and in which an afterburning of the only partially depleted fuel 50 to form a hot exhaust gas 60 takes place.

In accordance with the invention, the disc-shaped solid electrolyte 30 contains electron conducting components which cause an ohmic loss, as well as ion conducting components. The quantity ratio of these components is such that in an idling operating state of the battery 1, heat transfer from the cells to the environment can be compensated for by the ohmic loss. In the case of a lack of need for electrical power, the feeding of the reactants 40, 50 into the fuel cells 2 is maintained at a low level, so that the temperature in the cells 2 remains high in this idling operating state. This temperature should be so high that a transfer from the idling operating state into the energy delivering normal operation is possible within a pre-determinable length of time. This length of time amounts to ten minutes for example, preferably less than one minute. In the energy delivering operation (electrical power approximately 1W: heating power approximately 1.5 W) the outside of the battery 1 should not be warmer than approximately 30° C and in the idling state (heating power approximately 0.05 W; heating power approximately 0.3W) it should be less warm, for example 25°C. Thus in the idling state the temperature of the cells 2 is less than in the energy delivering normal operating state. The difference between the temperatures in the normal operating state and in the idling state is preferably less than 100 K.

The solid electrolyte with mixed conduction can be made of $Sr_4Fe_6O_{13}$, which is doped with La and/or Ti; it can be a perovskite of the composition (La, Sr)(Co, Fe)O_3; or preferably cerium oxide $CeO_{2-\epsilon}$ ($\epsilon \leq 0.2$), which

is doped with Gd, Y and/or Sm. The transference number of the oxygen ions during simultaneous transport of oxygen ions and electrons has to assume a value between 0.6 and 0.9. (The transference number - shows the ratio between the current of the oxygen ions and that of the electrons). In this arrangement the transference number has to be measured at operating temperature.

The battery in accordance with the invention advantageously includes a condenser 7, in particular a super-condenser (see Figures 1 and 3), by means of which the peaks of the power requirement, which as a rule occur intermittently, can be covered.

The fuel 50 is advantageously butane or propane. The battery 1 has a capacity determined by the amount of fuel. With a full fuel reservoir 5, the capacity of the battery 1 is at least 3,000 mAh. The fuel cells 2 connected in series produce a terminal voltage of 3.6 V. The battery has a diameter between 2 and 3 cm and a height between 2.5 and 3.5 cm.

Fig. 6 shows a schematic representation of an apparatus 4 for transporting the air 40, which is sucked in at an inlet point 40'. Two containers 44 and 46 of different size, which are designed like bellows, which are coupled by rigid connections 43 and 45 and the volumes of which can be altered between a minimum volume, which is almost zero, and a maximum volume, are used for sucking in. The volumes change in opposition to one another. In a first step the larger container 46 is filled with exhaust gas 60 from the battery: valve 61 open; valve 62 closed; volume flow V_1'; pressure p_1. Air 40 is transported into the battery 1 from the smaller, rigidly coupled container 44: non-return valve 41a is closed, non-return valve 41b is open; volume flow V_2'; pressure p_2. At the same time V_2' is $< V_1'$; $p_2 > p_1$. The interior pressure of the battery p_1 is greater than the

environmental pressure. The air 40 absorbs heat in the battery 1, wherein a volume increase and pressure rise occurs. The chemical reactions, which take place in the battery (electrode reactions, afterburning) likewise contribute to an increase in volume and rise in pressure. In a second step the larger container 46 is emptied: valve 61 closed; valve 62 open. Coupled with this air 40 is sucked in from the environment through the container 44. The exhaust gas 60 leaves the apparatus 4 at an exit point 60'. The air 40 which has been supplied is pre-heated in two heat exchangers 6a and 6b with the exhaust gas 60 transported in the counter-flow.

Further mechanisms for feeding the air 40 into the electrode gas chambers are possible. It is generally applicable that an overpressure p_2 or p_1 is produced in the gas-filled fuel cells 2 and channels by means of organs, which can act on the transport of the air and the exhaust gas. In this way the air supplied as a heat sink and as a reactant together with the fuel, has a thermodynamic working effect on the gases. A part of the pressure energy, which is stored in the exhaust gas, is used in this to transport the air through the apparatus. A further example for a transport apparatus of this kind is a "quasi gas turbine". Air is sucked in with a first micro-turbine. The second micro-turbine drives the first one. The exhaust gas flows away via the second micro-turbine while generating work. The reaction and combustion chambers of the battery have the function of a combustion chamber in a gas turbine in this arrangement. A method for the manufacture of micro-turbines is described in US-A-6 363 712 (Sniegowski et al).

The battery 1 in accordance with the invention can be used as a mobile energy source for electronic devices, which require a relatively high and regular energy supply. It can also be used as a substitute for rechargeable loadable batteries.